Cobalt-doped gahnite synthesized by hydrothermal method

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$Zn_{1-x}Co_xAl_2O_4$ (x = 0.05 and 0.1) pigment was synthesized by hydrothermal method and then annealed at 1000ºC. The samples prepared by hydrothermal method exhibit a green colour specific for octahedrally coordinated Co^{3+} ions. After annealing at 1000ºC, samples changed the colour from green to blue which is the specific colour for tetrahedrally coordinated Co^{2+} ions. The X-ray diffraction analysis showed a single spinel phase and no trace of impurities. The average crystallite size was found to be around 40 nm (x = 0.05) and 38 nm (x = 0.1). Atomic force microscopy measurements confirmed the nanosize of the particle. Absorbance spectra showed three peaks centered at 620, 593 and 547 nm attributed to the $^4A_2(F) \rightarrow {}^4T_1(P)$ transition.

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1. Introduction

Ceramic pigments present a high interest due to their applications in tableware, glasses, tiles and sanitaryware [1]. The most important properties of pigments are light absorption and particle size. The most appropriate particle size for pigments is between 1 and 10 μm [2]. Spinel type materials present these properties. Between spinels, gahnite is one of the most important. Gahnite has a normal spinel structure of the general formula AB_2O_4, where A may be Zn and B can be Al ions and belongs to the Fd3m spatial group [3-6]. Thus, in this system, zinc ions occupy tetrahedral sites and aluminium ions occupy octahedral sites. Gahnite spinel may be synthesized by various methods, such as: coprecipitation [7,8], hydrothermal [4,5,9], sol-gel [10,11], combustion [12], and so on. For ceramic pigments application, gahnite may be doped with transition ions (Cr, Mn, Co, Ni) or rare earth ions (Eu, Tb, Ce) [1]. Between this ion, Co^{2+} ion which occupies tetrahedral sites presents high interest [13,14]. Co^{2+} ions will occupy tetrahedral sites in the $ZnAl_2O_4$ system. The new formed system will exhibit a blue colour.

This paper presents the synthesis of Co-doped gahnite pigment by hydrothermal method and then annealed at 1000ºC and their characterization.

2. Experimental procedure

$Zn_{1-x}Co_xAl_2O_4$ (x = 0.05 and 0.1) spinel was synthesized by hydrothermal method. As precursors zinc nitrate hexahydrate, aluminium nitrate nonahydrate and cobalt chloride were used. Water solution of ammonia (25%) was used as precipitating agent. The precursors were dissolved in water and then mixed. The resulting pink precipitate was then transferred into a Teflon-lined stainless steel autoclave. The autoclave was kept at 220ºC for 8 hours, then the resulting green powder was filtered, washed and then dried. After drying the powder was annealed at 1000ºC for 3 hours. The colour has changed from green to blue.

The blue pigment was then characterize by means of X-ray diffraction using a X-ray powder diffractometer (PANalytical X'Pert Pro) with monochromatic Cu Kα (k = 1.5418 Å) incident radiation. Atomic force microcopy was made using the atomic force microscopy (Nanosurf® EasyScan 2 Advanced Research (AFM)). Infrared spectrum was recorded on a Bruker system Vertex 70 spectrophotometer using KBr pellet method. UV/VIS/NIR spectrophotometer (Model Lambda 950) was used to analyze the optical properties of the samples.

3. Results and discussions

In Fig. 1 X-ray diffraction pattern of $Zn_{1-x}Co_xAl_2O_4$ pigment is presented. The samples showed single spinel phase with no impurity trace (JCPDS 05-0669). The colour of the samples was green, which means that cobalt ions suffered a partial oxidation and Co^{3+} ions are situated in octahedral sites [15]. Because of this, the samples were annealed at 1000ºC for 3 hours.

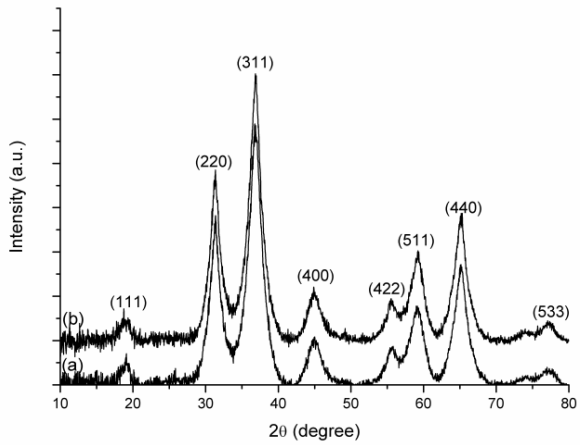

Fig. 1. X-ray diffraction pattern for $Zn_{1-x}Co_xAl_2O_4$ pigment where x = 0.05 (a), x = 0.1 (b).

In Fig. 2 we can see the patterns of the samples after annealing at 1000ºC. All diffraction peaks are indexed to a single spinel phase (JCPDS 05-0669). The $Zn_{1-x}Co_xAl_2O_4$ samples present a small shift of diffraction peaks. It can be seen that some diffraction peaks splits in comparison with the undoped sample which was reported in our previous work [16]. This split is reduced when the concentration of Co^{2+} ions increases. The annealed samples exhibit a blue colour. The blue colour is typical for tetrahedral - coordinated Co^{2+} ions [17].

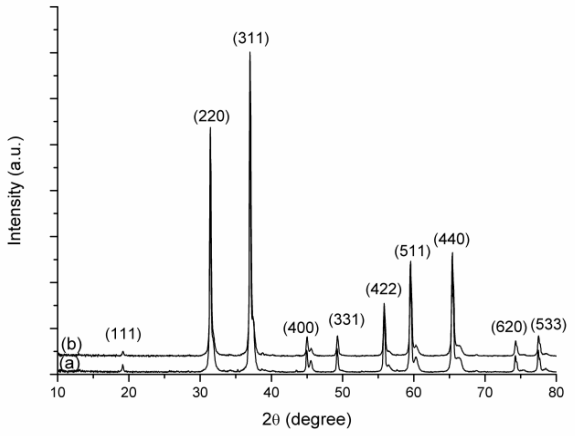

Fig. 2. X-ray diffraction pattern for $Zn_{1-x}Co_xAl_2O_4$ pigment where x = 0.05 (a), x = 0.1 (b) annealed at 1000ºC.

Using Scherrer's equation [18] the average crystallite size was determined. The average crystallite size decreases when the cobalt concentration increases. For the sample with x = 0.05 the average crystallite size was found to be around 40 nm while in case when x = 0.1 was found to be around 38 nm.

Atomic force microscopy (AFM) measurements were made using the contact mode cantilever. In Fig. 3 we can see the AFM images for $Zn_{1-x}Co_xAl_2O_4$ (x = 0.05 and 0.1) pigment. From AFM measurements it was determined that the particle size is around 48 nm (x = 0.05) and 42 nm (x = 0.1). The AFM results are in agreement with those from X-ray diffraction.

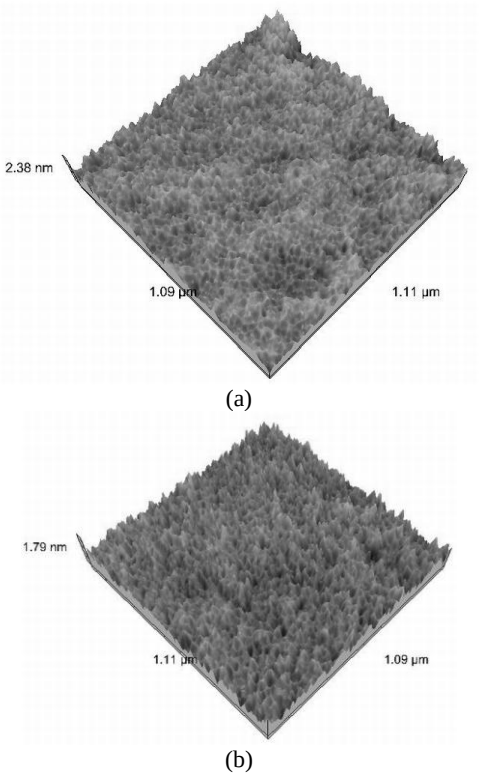

Fig. 3. AFM images of $Zn_{1-x}Co_xAl_2O_4$ pigment where x = 0.05 (a), and x = 0.1 (b) annealed at 1000ºC.

Infrared analysis was made using KBr pellet method. FT-IR spectrum was measured in the region 400 – 4000 cm^{-1}. The peaks centered at 503, 563, 658 cm^{-1} can be attributed to the bending and to the stretching mode of O-Al-O and Al-O in octahedral coordination state [8,19]. Peaks that appear at 1633 and 3435 cm^{-1} are attributed to the vibration mode of hydroxyl groups (OH) and to the deformation vibration of water molecule [20,21]. It was not found any trace of nitrates which means the samples are pure.

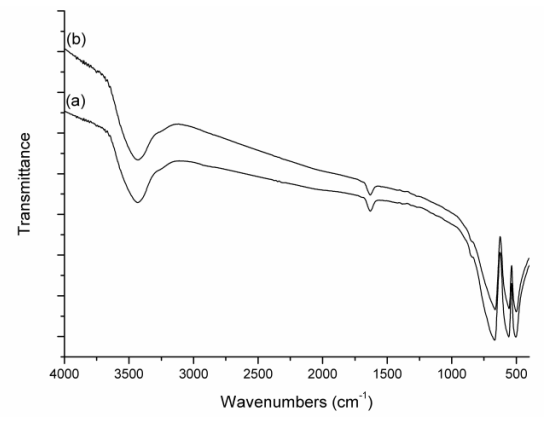

Fig. 4. FT-IR spectrum of $Zn_{1-x}Co_xAl_2O_4$ pigment where x = 0.05 (a), x = 0.1 (b) annealed at 1000ºC.

Optical properties of $Zn_{1-x}Co_xAl_2O_4$ pigment were analyzed by means of UV/VIS/NIR spectroscopy. Optical absorbance spectrum was determined by diffuse reflectance in the region 250-700 nm range at room temperature. In Fig. 5 the absorbance spectrum of $Zn_{1-x}Co_xAl_2O_4$ pigment is presented. As we can see, the absorbance spectrum reveals three strong peaks in the region 500-700 nm. The peaks centered at 620, 593 and 547 nm may be attributed to the $^4A_2(F) \rightarrow {}^4T_1(P)$ [22,23]. This transition is a typical transition of tetrahedrally coordinated Co^{2+} ions [3].

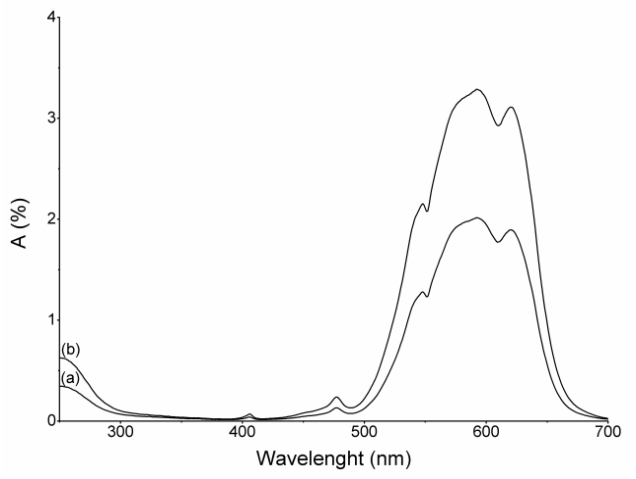

Fig. 5. Absorbance spectra of $Zn_{1-x}Co_xAl_2O_4$ pigment where x = 0.05 (a), x = 0.1 (b) annealed at 1000ºC.

Thus, optical absorbance spectra of $Zn_{1-x}Co_xAl_2O_4$ pigments confirmed the presence of tetraedrally coordinated Co^{2+} ions. Also, it can be seen that the intensity of absorbance spectra increases with the concentration of cobalt ions.

Fig. 6 presents the colour exhibited for both samples. It can be seen that the sample with x = 0.1 (right) shows a more intense colour that the one with x = 0.05 (left).

Fig. 6. Image of $Zn_{1-x}Co_xAl_2O_4$ pigment where x = 0.05 (left), x = 0.1 (right) annealed at 1000 ºC.

4. Conclusions

Co-doped $ZnAl_2O_4$ was synthesized by hydrothermal method and then annealed at 1000ºC. The samples obtained by hydrothermal method was green colored because of the partial oxidation of Co^{2+} in Co^{3+} ions. The colour changed from green to blue when the samples were annealed at 1000ºC. The Co-doped $ZnAl_2O_4$ presents a single spinel phase and the average crystallite size was found to be 40 nm (x = 0.05) and 38 nm (x = 0.1). AFM measurements confirmed these results. FT-IR spectra revealed the purity of the obtained samples. Absorbance spectra confirmed the presence of tetrahedrally coordinated Co^{2+} ions.

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